

80. (New) The method of claim 79 wherein exposing the first conductive layer comprises exposing the first conductive layer to a selection of B_2H_6 , PH_3 , CH_3SiH_3 , $(CH_3)_3Si-Si(CH_3)_3$, HMDS, CF_4 , CHF_3 , HCL , BCl_3 , and SiH_4 gases, and combinations thereof *in situ*.

81. (New) The method of claim 79 wherein exposing the first conductive layer comprises exposing the first conductive layer to a selection of B_2H_6 , PH_3 , CH_3SiH_3 , $(CH_3)_3Si-Si(CH_3)_3$, HMDS, CF_4 , CHF_3 , HCL , BCl_3 , and SiH_4 gases, and combinations thereof *ex situ*.

REMARKS

Claims 17-24 and newly added claims 76-81 are currently pending in the present application. In the Office Action mailed September 13, 2001, the Examiner rejected claims 17, 18, and 20-24 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent No. 5,670,808 to Nishihori *et al.* ("Nishihori"). The Examiner also objected to claim 19 as being dependent upon a rejected base claim but indicated claim 19 would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. Claim 19 has been rewritten in independent form and is therefore now allowable.


The Examiner also objected to claims 21 and 24 under 37 C.F.R. § 1.75 as being duplicates of claims 20 and 23, respectively. The Examiner states he "understands that the phrase 'exposing said first conductive layer to a passivation gas *in situ*' in claim 20 and the phrase 'exposing said first conductive layer to a passivation gas while still in said first environment' in claim 21 mean the same." The term *in situ* as used in the art means in the same chamber or in the same physical location, but not necessarily in the same atmosphere in that chamber. Thus, the phrase "exposing said first conductive layer to a passivation gas *in situ*" in claim 20 is broader than the phrase "exposing said first conductive layer to a passivation gas while still in said first environment" in claim 21 since in claim 20 the first conductive layer is exposed *in situ* but not necessarily in the first environment. Accordingly, claim 20 and 21 are not duplicates and this objection should be withdrawn.

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With regard to claims 23 and 24, the Examiner states he "understands that the phrases "oxygen free environment" in claim 23 and "a second oxygen free environment" in claim 24 mean the same as there is no reference to a first oxygen free environment." Claim 24 depends from claim 22 which recites "an oxygen-free environment" that corresponds to a first oxygen-free environment. Thus, in claim 23 the second conductive layer is deposited in the first oxygen-free environment recited in claim 22 while in claim 24 the second conductive layer is deposited in the second oxygen-free environment recited in claim 24. Claims 23 and 24 are thus not duplicates and this objection should be withdrawn.

Applicant's invention exposes a conductive layer to an oxygen-inhibiting plasma or other gas, including nitrogen free gases, prior to the formation of the another layer or layers on the conductive layer to substantially reduce the association of oxygen with the conductive layer during formation of the other layer or layers. By reducing the amount of oxygen associated with the conductive layer, the electrical characteristics of a semiconductor device including the conductive layer are improved, as will be discussed in more detail below with reference to the disclosed embodiments of the invention. In order to help the Examiner appreciate certain distinctions between the pending claims and the subject matter of the applied reference, the disclosed embodiments of the invention will now be discussed in comparison to the applied reference. Specific distinctions between the pending claims and the applied references will be discussed after the discussion of the disclosed embodiments and the applied reference. This discussion of the differences between the disclosed embodiments and applied reference does not define the scope or interpretation of any of the claims.


One embodiment of the present invention is discussed with reference to Figures 7-10 in which an interposing layer 52 such as a tungsten nitride layer 52 is formed between a conductive plug 46 formed in a via 44 and a conductive line material 48 formed in a trench or container 50. The tungsten nitride layer 52 enhances the electrical contact between the line material and the plug, promotes adhesion of the line material within the container 50, prevents or slows the diffusion of materials across the tungsten nitride layer boundary, or serves some other purpose. As previously described, the tungsten nitride layer 52 may associate with oxygen after it is formed and subsequent thermal processes may result in the formation of an oxide layer 54 formed between the tungsten nitride layer 52 and the line material 48. Because the oxide layer



54 is an insulator, this layer will adversely affect the electrical connection between the line material 48 and the plug 46. By exposing the tungsten nitride layer 52 to an oxygen-inhibiting agent or a reducing atmosphere prior to formation of the line material 48, the thickness of the oxide layer 54 is reduced to a thickness of less than 10 angstroms or entirely eliminated as illustrated respectively in Figures 9 and 10. Thus, in all embodiments a conductive layer is exposed to an oxygen-inhibiting agent or reducing atmosphere prior to another layer being formed on the conductive layer to thereby reduce an ability of the conductive material to associate with oxygen.

As described in the specification, the tungsten nitride layer 52 or other conductive layer may be treated in a plasma such as an N_2 and H_2 plasma, an NH_3 plasma, or an N_2 plasma. See page 6, lines 13-30 and page 7, lines 1-19. Furthermore, the conductive layer may be treated in a nitrogen-free gas, such as a plasma treatment including H_2 or other gases such as diborane B_2H_6 , PH_3 , CH_3SiH_3 , $(CH_3)_3Si-Si(CH_3)_3$, HMDS, CF_4 , CHF_3 , HCL , BCl_3 , and silane SiH_4 , and any combinations of these gases, as described on page 7, lines 25-30, page 8, lines 1-16, and page 9, lines 1-12. As will be appreciated by those skilled in the art, the use of a plasma treatment enables energy of ions forming the plasma to be closely controlled to thereby more precisely treat the tungsten nitride layer as desired. Moreover, the other nitrogen-free gases provide beneficial treatment of the conductive layer when compared to nitriding of the layer by exposure to a nitrogen containing gas and the associated heat treatment.

Another embodiment of the present invention is illustrated in Figures 4 and 5 that depict an in-process semiconductor device. As mentioned in the specification, for the purposes of explanation the in-process semiconductor device is assumed to be a capacitor in the process of being constructed. In Figure 4, the capacitor includes a first conductive layer or 24, which may be formed from hemispherical silicon grain (HSG), formed over a substrate 22, and a dielectric 26 formed on the first conductive layer. In the examples of Figures 4 and 5, the dielectric 26 is formed from tantalum pentoxide Ta_2O_5 . A second conductive layer 28 formed from tungsten nitride WN_x is then formed on the dielectric 26. The tungsten nitride layer 28 has a tendency to associate with oxygen, particularly if that layer is exposed to oxygen prior to a third conductive polysilicon layer 30 being formed on the tungsten nitride layer 28. During subsequent processing of the capacitor, the oxygen contained in the tungsten nitride layer 28 can combine



with silicon from the polysilicon layer 30 to form an unwanted silicon dioxide layer 36 between the tungsten nitride layer 28 and the polysilicon layer 30. For example, a thermal process step such as the formation of a borophosphosilicate glass (BPSG) layer 34 over the polysilicon layer 30, which of course occurs after the formation of the polysilicon layer 30, may cause a reaction between the polysilicon layer 30 and the oxygen in the tungsten nitride layer 28 and thereby form the silicon dioxide layer 36.

Ideally, the HSG layer 24 forms a first plate of the capacitor, the tantalum pentoxide 26 forms the dielectric of the capacitor, and the tungsten nitride layer 28 and polysilicon layer 30 form the second plate of the capacitor. With the formation of silicon dioxide layer 36, however, the capacitor now includes a first capacitor corresponding to the HSG layer 24, tantalum pentoxide 26, and tungsten nitride layer 28, and a second capacitor in series with the first capacitor, with the second capacitor corresponding to the tungsten nitride layer 28, silicon dioxide layer 36, and polysilicon layer 30. These first and second capacitors connected in series have a combined capacitance that is less than that of the ideally formed capacitor. As will be understood by those skilled in the art, the thickness of the silicon dioxide layer 36 affects the value of the combined capacitance.

In the capacitor of Figure 4, the thickness of the silicon dioxide layer 36 is greatly reduced by exposing the tungsten nitride layer 28 to an oxygen-inhibiting agent prior to the formation of the polysilicon layer 30 to thereby greatly reduce the association of the tungsten nitride layer with oxygen. The silicon dioxide layer 36 in the embodiment of Figure 4 is less than 10 angstroms thick due to the oxygen-inhibiting agent, while in a conventional capacitor shown in Figure 3 the silicon dioxide layer 36 is about 10-40 angstroms thick. In the capacitor of Figure 5, the exposure of the tungsten nitride layer 28 to the oxygen-inhibiting agent eliminates the formation of the silicon dioxide layer 36 altogether.

The oxygen-inhibiting agent may be an N_2 and H_2 plasma, with the tungsten nitride layer 28 ideally being exposed to this plasma prior to exposing tungsten nitride layer to an atmosphere associated with the formation of the polysilicon layer 30 or prior to exposing the tungsten nitride layer to oxygen. As described in the specification, it is believed the exposure of the tungsten nitride layer 28 to the N_2 and H_2 plasma or any of the other oxygen-inhibiting agents stuffs the tungsten nitride layer grain boundaries with nitrogen or otherwise passivates the

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tungsten nitride layer, making the bonds at the grain boundaries less active and less likely to associate with oxygen. It should be noted that even if the tungsten nitride layer 28 is exposed oxygen, the layer may thereafter be exposed to a reducing atmosphere, such as silane gas SiH_4 , prior to formation of the polysilicon layer 30 to thereby reduce the oxygen content of the tungsten nitride layer 28 and reduce the thickness of any silicon dioxide layer 36 thereafter formed.

In another embodiment of the present invention discussed with reference to Figure 6, a first conductive layer such as a tungsten nitride layer 128 is deposited over a substrate 122 and a dielectric layer 126, such as a tantalum pentoxide layer, is deposited over the tungsten nitride layer. In this situation, the deposition of the tantalum pentoxide layer 126 may cause the tungsten nitride layer 128 to incorporate oxygen, reducing the capacitance of a capacitor including the tungsten nitride layer and tantalum pentoxide layer. Accordingly, in this embodiment of the invention, the tungsten nitride layer 128 is exposed to a N_2 and H_2 plasma or other oxygen-inhibiting agent before depositing the tantalum pentoxide layer 126. As previously described, the N_2 and H_2 plasma passivates the tungsten nitride layer 128 to thereby prevent oxygen from being incorporated within the tungsten nitride layer.

The Nishihori patent discloses a semiconductor device including a capacitor having an electrode that is processed in a nitrogen atmosphere to prevent oxidation of a surface of the electrode and thereby prevent the formation of an unwanted dielectric layer that reduces the capacitance of the capacitor. Figure 1 illustrates a capacitor 10 including a lower electrode 14 including a Ti layer, Mo layer, and Pt layer formed in this order from bottom to top. A dielectric film 15a is formed on the lower electrode 14, and an upper electrode 16a having a WN_x layer and W layer formed in this order from bottom to top is formed on the dielectric film. Figures 12A-12C are cross-sectional views illustrating a method of manufacturing the capacitor 10 of Figure 1.

Figure 12A illustrates a first step of the process in which a WN_x film that will be processed to form a lower electrode 43 is formed on a silicon dioxide film 42 arranged on a semiconductor substrate 41. A heat treatment is thereafter performed in an ammonia NH_3 gas atmosphere to achieve a predetermined nitriding rate in the lower electrode 43. During the heat treatment, nitrogen diffuses into the surface of the lower electrode 43, which further increases the

nitriding rate and improves the oxidation resistance of the lower electrode. See column 9, lines 37-39. In this way, the specification states "it is possible to hardly produce and oxide [between the lower electrode 43 and a dielectric film 44 subsequently formed on the lower electrode] which lowers the capacitance of the capacitor [10]." See column 9, lines 38-42. In all embodiments in Nishihori, the heat treatment of the lower electrode is in a gas containing nitrogen. See column 9, lines 33-35, column 11, lines 56-59, and column 10, line 12., as indicated in column 10, line 12. Figures 13-15 are graphs illustrating the nitriding rate of the lower electrode 43 as a function of capacitance, oxidation rate, and temperature. Moreover, Nishihori makes no disclosure nor suggestion to utilize a plasma or a nitrogen free gas, such as B_2H_6 or silane, in treating the lower electrode 43. As previously described, utilization of a plasma in the present invention allows the energy of ions forming the plasma to be closely controlled to thereby more precisely treat the tungsten nitride layer as desired. Nishihori discloses and suggests only one way of improving the oxidation resistance of the lower electrode 43, namely nitriding the electrode via heat treatment in a nitrogen-containing environment.

Amended claim 17 recites a method of forming a capacitor including forming a capacitor plate, which includes providing a first conductive layer in a first environment, exposing said first conductive layer to a nitrogen free passivation gas, and depositing a second conductive layer over said first conductive layer. Nishihori neither discloses nor suggests exposing the first conductive layer to a nitrogen free passivation gas as previously discussed. The combination of elements recited in claim 17 is therefore allowable, and dependent claims 18 and 20-24 are allowable for at least the same reasons as claim 17.

New claim 76 recites a method of forming a capacitor including forming a capacitor plate, which includes providing a first conductive layer in a first environment, exposing the first conductive layer to a plasma in a second environment, and depositing a second conductive layer over the first conductive layer. Nishihori neither discloses nor suggests exposing the first conductive layer to a plasma in a second environment. The combination of elements recited in new claim 76 is therefore allowable, and dependent claims 77-78 are allowable for at least the same reasons as claim 76.

New claim 79 recites a method of forming a capacitor including forming a capacitor plate, which includes providing a first conductive layer in a first environment, exposing

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the claims:

Claims 17-22 and 24 have been amended as follows:

17. (Amended) A method of forming a capacitor, comprising:
 forming a capacitor plate, comprising:
 providing a first conductive layer in a first environment;
 exposing said first conductive layer to a nitrogen free passivation
 gas; and
 depositing a second conductive layer over said first conductive
 layer.

18. (Amended) The method in claim 17, wherein said step of exposing said
 first conductive layer to a nitrogen free passivation gas further comprises exposing said first
 conductive layer to a nitrogen free passivation gas *ex situ*.

19. (Amended) A method of forming a capacitor, comprising:
 forming a capacitor plate, comprising:
 providing a first conductive layer in a first environment;
 exposing said first conductive layer to a passivation gas; [The
 method in claim 17,] wherein said step of exposing said first conductive layer to a passivation
 gas further comprises exposing said first conductive layer to silane in a second environment; and
 depositing a second conductive layer over said first conductive
 layer.

20. (Amended) The method in claim 17, wherein said step of exposing said
 first conductive layer comprises exposing said first conductive layer to a nitrogen free
 passivation gas *in situ*.

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21. (Amended) The method in claim 17, wherein said step of exposing said first conductive layer comprises exposing said first conductive layer to a nitrogen free passivation gas while still in said first environment.

22. (Amended) The method in claim 17, wherein said step of providing a first conductive layer comprises providing a first conductive layer in an oxygen-free environment; and wherein said step of exposing said first conductive layer comprises exposing said first conductive layer to a nitrogen free passivation gas in said oxygen-free environment.

24. (Amended) The method in claim 22, wherein said step of depositing a second conductive layer comprises depositing said second conductive layer in a second [oxygen] nitrogen free-environment.

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